

Heterogeneous Batch Distillation Processes: Real System Optimisation

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ACCEPTED FOR PUBLICATION in

Chemical Engineering and Processing, 47(3), 408-419, 2008 .

Abstract

In this paper, optimisation of batch distillation processes is considered. It deals with real systems with rigorous simulation of the processes through the resolution full MESH differential algebraic equations. Specific software architecture is developed, based on the BatchColumn® simulator and on both SQP and GA numerical algorithms, and is able to optimise sequential batch columns as long as the column transitions are set.

The efficiency of the proposed optimisation tool is illustrated by two case studies. The first one concerns heterogeneous batch solvent recovery in a single distillation column and shows that significant economical gains are obtained along with improved process conditions. Case two concerns the optimisation of two sequential homogeneous batch distillation columns and demonstrates the capacity to optimize several sequential dynamic different processes. For such multiobjective complex problems, GA is preferred to SQP that is able to improve specific GA solutions.

Keywords: Optimisation, Batch Distillation, Heterogeneous Azeotrope, Batch distillation sequence

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1. Introduction

Solvent recovery is a major issue in the pharmaceutical and specialty chemical industries. In that purpose, batch distillation is a separation process of choice. For azeotropic or close-boiling mixtures, the addition of an entrainer, partially or totally miscible with one of the initial binary mixture components, is viable and its choice is the first key issue of azeotropic batch distillation. A whole set of entrainer selection rules has been published for both homogeneous and heterogeneous azeotropic distillation for the separation of azeotropic binary mixtures or close boiling components (Rodríguez Donis *et al.*, 2001a and 2001b, Skouras *et al.*, 2005b). These rules also hint at a feasible sequence of batch column needed to perform the separation together with the initial feed stream location in the ternary diagram. But the optimisation of the column sequence is a second key issue and this contribution validates a framework for the optimisation of such a complex batch distillation process.

No optimisation of batch distillation of a heterogeneous mixture was published hitherto, nor any optimisation of a sequence of batch distillation columns, showing the originality of our contribution.

The paper is organised as follow: an overview of batch distillation optimisation published in the literature is presented. Then, the optimisation problem is defined: objective function, constraints and optimisation variables. The paper proceeds with a presentation of the software architecture implemented and with a presentation of the stochastic and deterministic optimisation methods used. Then three sections are devoted to the validation of the optimisation framework: first, optimisation of a simple batch distillation without rigorous thermodynamic Models and equation; second, optimisation of a real heterogeneous batch distillation column and comparison with the feasibility analysis predictions; and third, optimisation of a two batch distillation columns sequence illustrating the capability of the framework to optimise several and different batch distillation columns linked by a so-called column transition.

2. Background on batch distillation optimisation

The optimisation of batch distillation processes has been widely studied in the literature. The general objective is to determine the optimal Strategy based on a given objective function and satisfying several constraints. In particular, the goal is to determine the optimal reflux policy to obtain a specified quality of product. The optimisation problems studied in the literature go from the simplest to the most complex ones. In addition to the type of process structure or of operation Mode, the problems differ by

the types of thermodynamic mixtures handled (generally 2 or 3 components forming an ideal zeotropic homogeneous mixture).

2.1. Formulation of a batch distillation optimisation problem

Three categories of batch distillation optimisation problems are found in the literature:

1. Problem of maximum distillate which aims at maximizing the quantity of distillate recovered with a given purity in a given time.
2. Problem of minimum time which aims at minimizing the total operation time to produce a given quantity of distillate with a given purity.
3. Problem of maximum profit which aims at optimizing an economic cost function to includes many contributions like the total operation time, the quantity of distillate, its purity...

In the tool we present, these three criteria are indifferently used according to the choice of the problem to optimize. The third criterion is often set based a linear combination or a ratio of the first two criteria. Finally, depending on the criterion, the various problem constraints can be stated differently.

2.2 Batch distillation optimisation variables

The most used variable of action or of control is the reflux as it is often sought to set an optimal reflux policy enabling to obtain the various specifications of purity, time or quantity. Other optimisation variables can be taken into account such as the heat duty to the boiler (Fernholz *et al.*, 2000), the plate and tank holdup values (Furlonge *et al.*, 1997), the recycling flows (Lelkes *et al.*, 1998, Bonny *et al.*, 1996) and the operating conditions (Fraga *et al.*, 1996).

The majority of these optimisation variables are usually time dependent, conferring to the problem an infinite dimension. To transform it into a finite size problem, discretisation techniques with respect to time can be used. The time horizon is then cut out in a finite number of intervals: 2 (Sorensen and Skogestad, 1996), 4 (Noda *et al.*, 2001), 5 (Fernholz *et al.*, 1997), 6 (Mujtaba and Macchieto, 1996), 7 (Furlonge *et al.*, 1997) or 40 (Hanke and Li, 2000). This choice results from a compromise between precision from the discretisation and computing time. Several schemes of parameterisation can then be considered: Lagrange polynomials to describe a constant profile (order 1) or linear per part (order 2); exponential functions (Farhat *et al.*, 1989) or a combination of Lagrange - exponential function (Kim, 1999). Two types of discretisation with respect to time can be distinguished: the parameterisation of all variables or the parameterisation of the optimisation variables only. In the first case, integration of the DAE system modelling the batch distillation process is avoided, but the size of

the problem becomes very large. In the second case, the size of the problem is more reduced, but using of an efficient DAE integrator is necessary to handle to the complexity of the DAE set of equation. In both cases, new values of the optimisation variables are generated for each interval of time considered.

Finally, optimisation variables of integer type are sometimes considered, primarily in process design: number of theoretical stages, feed plate position, as well as a sequence of the batch tasks. They require a particular treatment in the methods of optimisation (MINLP) (Frey *et al.*, 1997). In particular cases, the number of stages is regarded as a continuous variable that is then transformed into an integer using appropriate computer functions (Mujtaba and Macchietto, 1996).

2.3 Solving methods of batch distillation optimisation problems

The methods of resolution of batch distillation optimisation problems depend on the type of optimisation variables and of the choice of the criterion, with or without explicit constraints. The presence or not of integer variables brings the optimisation problem into a different mathematical world (Mixed Integer Non Linear Programming vs. Non Linear Programming). The MINLP undoubtedly represents currently the highest degree of mathematical sophistication and is used for the design of distillation process (Nowak *et al.*, 1996, Frey *et al.*, 1997).

When only continuous/real variables are present, as it is in our case, various methods can be employed: dynamic programming (Coward, 1967), Pontryagin maximum principle (Farhat *et al.*, 1989, Betlem *et al.*, 1998), increased Lagrangian (Bonny *et al.*, 1994), generalized reduced gradient (Jang, 1993) and Sequential Quadratic Programming SQP (Noda *et al.*, 2001). All these optimisation techniques are deterministic methods. The use of SQP seems to be from now on a standard to deal with nonlinear problems of optimisation and it is available in most commercial libraries (IMSL, GAMS, MATLAB, etc...). Besides, a study of various commercial SQP was published to compare their performances according to various criteria such as the problem size, the accuracy of the solution or the computing time (Kao, 1998).

But stochastic methods of optimisation can also be used, among which Genetic Algorithm based methods (Fraga *et al.*, 1996, Mukherjee *et al.*, 2001) and simulated annealing methods (Hanke and Li, 2000) can be quoted. The choice of a deterministic or a stochastic method depends on their characteristics. In the first case, convergence towards an optimum requires a good starting point and often the knowledge of the gradients of the criterion and constraints which are explicit. In the second

case, mathematical implementation is much simpler, without gradient or any good initial point, but it requires a large number of calls to the objective function which requires in its turn to simulate of the process and it can only handle constraints implicitly in the objective function. Finally, to soften the disadvantages of each one of these methods, the use of a stochastic method as initialisation of a deterministic method seems to be a compromise worth consideration (Fraga and Zilinskas, 2003).

3. Batch distillation optimisation problem definition

We consider a batch distillation optimisation aiming at minimising an overall economical criterion while respecting constraints such as purity, recovery yield.... It can be considered as a nonlinear optimisation problem under constraints. The classical formulation involves an objective function f , equality constraints and inequality constraints (respectively g_i and h_j):

$$\begin{aligned} \text{Min } & f(x) \\ & g_i(x) = 0 \quad i = 1, \dots, n_g \\ & h_j(x) \leq 0 \quad j = 1, \dots, n_h \end{aligned} \quad (1)$$

The formulation is the same whatever the number of batch distillation columns that are considered in a batch distillation sequence.

3.1. Objective function

The objective function f is the summation of six cost functions c_i described in Table 1:

Table 1. Economical cost functions taken into account in the objective function

cost function	$f = \sum_{i=1}^6 c_i$	object	expression	used variable
c_1		immobilisation	$c_1 = a_1 \cdot t + b_1$	t = total separation duration
c_2		energy	$c_2 = a_2 \cdot Q$	Q = total required energy
c_3		load	$c_3 = a_3 \cdot L$	L = global column load
c_4		entrainer	$c_4 = a_4 \cdot E$	E = entrainer amount added initially
c_5		column treatment	$c_5 = a_5 \cdot R + b_5$	R = residual column load
c_6		tanks treatments	$c_6 = \sum_{k=1}^{n_T} a_6^k \cdot T_k + b_6^k$	T_k = final load of each of the n_T tanks (including still)

3.2. Constraints

The constraints of the NLP problem are defined with respect to target purity and/or quantity specifications at the end of the distillation process. Constraints can be expressed in any relevant unit (volume, mass and molar for the composition...) and may concern either internal tanks (boiler, condenser-decanter) or external production tanks.

Each constraint h_j (the same for g_i) is expressed as follows:

$$h_j = x_i^k - x_{i,obj}^k \quad (2)$$

where x_i^k and $x_{i,obj}^k$ are the effective and the target fraction of component i in tank k .

3.3. Optimisation variables

Optimisation variables are chosen among all the available running specifications of a batch distillation process, which is a collection of successive tasks and the initial load of entrainer in the first column (Table 2).

Table 2. Available optimisation variables

optimisation variable (* available for each task i)	
Entrainer load	Task duration *
Boiling duty *	Reflux ratio of light phase * [£]
Subcooling temperature *	Reflux ratio of heavy phase * [£]

£: in case of homoazeotropic distillation, these optimisation variables are replaced by the usual reflux ratio.

4. Problem resolution

4.1. Overall resolution software architecture

The proposed optimisation methodology lies on a rigorous simulation of the considered batch processes. Most of the variables values required to evaluate the objective function and the constraints are calculated through this process simulation. From a defined column configuration and defined initial settings, a full MESH (Material balance, Equilibrium, Summation of molar fraction, Heat Balance) set of differential algebraic equation is solved using the BatchColumn® software (ProSim SA, France).

Main results from the batch simulations are mass and composition in each distillate tank and in the boiler, as well as the total heating and cooling duties. The economical optimisation criterion and the constraints values are evaluated from these results. These evaluations stand for the heart of the resolution software architecture, as shown in Figure 1.

The software architecture is able to handle batch processes made of several batch columns, each described by a different and independent DAE set, that form a so-called column sequence, linked by so-called column transitions. Such sequences are mandatory for the separation of many azeotropic mixtures (Rodriguez-Donis *et al.*, 2001a and 2001b). The multi-column optimisation problem is set initially through a GUI Configuration Manager which describes the column sequence and the tank transitions between the columns; select the cost functions summing up to the objective function; defines the constraints; sets the optimisation tools parameters and sets the bounds of the optimisation variables.

The Optimisation Manager offers strategies to change the values of the optimisation variables in order to solve the constrained minimisation problem; either using stochastic (Genetic Algorithm) or deterministic (Sequential Quadratic Programming) methods.

The Execution Monitor aims at calculating the objective function and constraints and dialoguing with the Optimization Manager and with the BatchColumn® simulator, eventually managing the information relevant to each column transition between two column simulations.

The resolution sequence is sketched on Figure 1. It contains an iterative loop until solution is reached, centred on the Execution Monitor whereas final results are displayed in the GUI Configuration Manager.

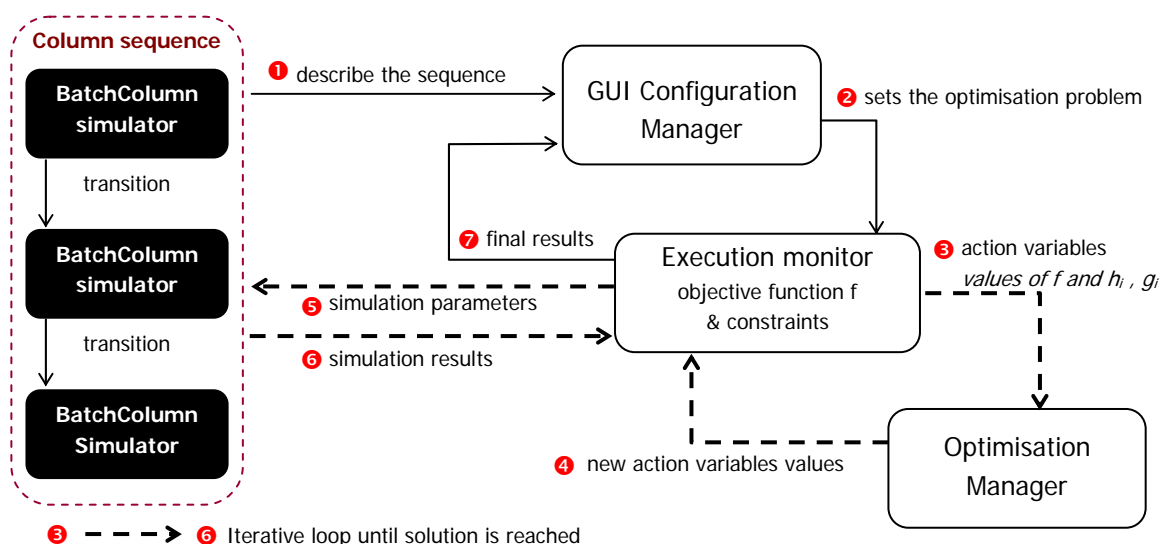


Figure 1. Optimisation software architecture and overall resolution scheme

4.2. Optimisation methods

Two optimisation techniques are used: a SQP-based deterministic method and a handmade Genetic Algorithm as a stochastic one.

The SQP algorithm is the *donlp2* tool, available at www.netlib.org (Spellucci, 1998a and 1998b). It incorporates the exact l1-merit function and a special Broyden Fletcher Goldfarb Shanno quasi-Newton approximation to the Hessian. The optimisation problem is strictly equation (1). Up to 17 different stop criteria are available in the *donlp2* tool, but the only one used are A1: the Kuhn-Tucker conditions (in particular a hessian matrix equal to zero within tolerance Epsx); A2: non evolution of the optimisation variables; A3: the non evolution of the objective function. Only A1 condition defines a strict optimum.

The genetic algorithm is real-coded. In order to use such an unconstrained optimisation technique, the constraints are introduced into the objective function by penalty terms. The optimisation problem aims then at finding the minimum of the following f_p penalized objective function:

$$f_p = f + \sum P_i \cdot (g_i)^2 + \sum Q_i \cdot (h_i)^2 \quad (3)$$

$$\text{with } P_i(x) = \begin{cases} 0 & \text{if } g_i(x) = 0 \\ P_i^0 & \text{if } g_i(x) \neq 0 \end{cases} \quad \text{and} \quad Q_i(x) = \begin{cases} 0 & \text{if } h_i(x) \leq 0 \\ Q_i^0 & \text{if } h_i(x) > 0 \end{cases}$$

and P_i^0 and Q_i^0 are weighting factors equal to the initial criteria value divided by the squared tolerances on the constraints. The GA stop criterion is defined by the maximum standard deviation allowed for the penalized objective function over a population of solutions generated by the GA.

5. Optimisation of an ideal binary mixture batch distillation process

5.1 Setting the optimisation problem

In order to investigate the influence of the numerical parameters of the GA and of the SQP on the solutions, we optimise a batch distillation process of two hypothetic compounds A and B. The distillation column DAE Model is taken from the literature (Sorensen and Skogestad, 1996). It is based on constant molar overflow hypothesis; therefore it has no energy balance, but only material balances on each of the 10 plates. Homogeneous liquid – vapour equilibrium are described by a fixed relative volatility, with A more volatile than B. The optimisation problem consists in maximizing the recovery

yield of A in the distillate tank, while keeping its purity above 95% molar as an inequality constraint. The distillation proceeds in two tasks, each with a different fixed reflux ratio.

In this numerical parameter study, the objective function to be minimized is the opposite of the A recovery yield in the distillate tank. The optimisation variables are the reflux ratio values R1 and R2 of the two tasks and the switch time t_{switch} between the two tasks. Initial values and bounds are set for each optimisation variables: the R1 and R2 are initially set at 0.5 and allowed to range between 0 and 1; t_{switch} initially equals unity and can range between 0 and 3 hours.

5.2 GA Parameter sensitivity analysis

For the reference run, the constraint tolerance is set to 0.001 and the convergence factor is set to 10^{-3} . Thus for the GA, the penalized weighting factor equals 10^6 . The GA selection rate and mutation rate are set respectively to 0.5 and 0.05 and a 100 people initial population is considered.

The most significant results of the parameter sensitivity analysis are summarized in Table 3. For the reference set and for each parameter study, 10 different runs are performed and the mean value is given in Table 3.

Table 3. Parameter sensitivity analysis on the GA optimisation results

Genetic Algorithm	Initial conditions	Reference set	Initial population		Selection rate	Mutation rate	Penalized weighting factor	
			10	1000	0.8	0.01	10^3	10^8
$t_{\text{switch}} \text{ (hr)}$	1	1.42	1.38	1.57	1.20	1.51	1.66	1,58
R_1	0.5	0.82	0.74	0.82	0.82	0.83	0.82	0,82
R_2	0.5	0.88	0.86	0.89	0.89	0.89	0.90	0,89
Objective function $f = -A \text{ recovery yield}$	0.99	4.267	4.872	4.348	4.260	4.170	4.400	4,260
$h_1(x_A) (>0.950)$	0.501	0.952	0.841	0.950	0.953	0.959	0.945	0,955
Population number	-	28	20	30	9	26	20	29
Objective function evaluation number	-	1723	120	18814	956	1521	1247	1806

It is observed that the optimization computer time proportional to the number of evaluation of the objective function is proportional to the initial population. If this latter is too small, the purity constraint

cannot be satisfied. The same happens if the tolerance on the constraint is not strict enough as shown in the last column relative to the penalized weighting factor. The GA selection rate can be safely increased to 0.8 and it reduces the computer time significantly while achieving the same performance as with the reference selection rate of 0.5. Decreasing the GA selection rate achieves even better performance but to the expense of a larger computer time. The GA mutation rate has almost no influence but a smaller value (0.01) than the reference value of 0.05 degrades slightly the recovery yield.

Besides, it may happen that the execution monitor requests the evaluation of the objective function and of the constraints outside their definition range, leading to a non converging simulation. In that case that happens while the AG is generating a population of solutions, the AG simply discards the simulation and runs another one instead.

5.3 SQP Parameter sensitivity analysis

The SQP parameter sensitivity analysis most significant results are summarized in Table 4. Many parameters can be varied, but only the overall tolerance on the Kuhn-Tucker conditions $Epsx$ and the initial conditions are displayed. Other parameters were tested but are not displayed: when the tolerance under which the constraints are taken into account is low, constraints are more strictly satisfied but at the expense of a larger number of evaluation of the constraint and of the objective function. The parameter defining the region where the constraints are not satisfied but the variables can enter during the search of a solution does not show any significant influence on the results even though it affect the strategy of evolution of the variables during the SQP search.

Table 4. Parameter sensitivity analysis on the SQP optimisation results

Sequential Quadratic Programming	GA Reference set	Best SQP result	$Epsx$
t_{switch} (hr)	1.42	1.695	1.697
R_1	0.82	0.821	0.822
R_1	0.88	0.897	0.897
Objective function $f = -A$ recovery yield	4.267	4.356	4.354
$h_1(x_A)$ (>0.950)	0.952	0.95020	0.95000
Constraint evaluation number	28*	99	203
Objective function evaluation number	1723	148	262

<i>Stop condition</i>	-	<i>A2</i>	<i>A3 (A1 condition satisfied)</i>
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* Population number

With a Epsx parameter value equal to 10^{-3} , the best SQP results are slightly better than the AG reference set but far less demanding in terms of computing time. In particular, the constraints are satisfied within the Epsx value. Increasing Epsx does degrade the optimal solution but decreasing it affects the stop conditions as the Kuhn-Tucker condition A1 is then systematically satisfied and the algorithm because of non evolution of the optimisation variables and of the objective function.

When the initial conditions are varied, three tendencies are observed:

- Convergence towards a solution close to the optimal solution. This happens for all initial points near the optimal solution, that satisfy some of the constraints.
- Convergence towards a non optimal solution. This happens for all initial points far from the optimal solution and is a well known drawback of deterministic optimisation methods. But it also happens when the switch time is set at one of its bounds, reducing the process to a single distillation task.
- No convergence. This happens for 10% of the cases when the initial points are far from the optimal solution.

These observations confirm the well known sensitivity of SQP tools to initial conditions that should at least satisfy some of the constraints.

Besides, In the case that the execution monitor requests the evaluation of the objective function and of the constraints outside their definition range, the SQP is set so as to handle such failure and eventually request other simulations to evaluate correctly the objective function.

Overall, this parameter analysis shows that the SQP is more performant than the AG to find an optimal solution. but it requires careful initialisation, a drawback not significant for the AG.

6. Case study one. Separation of Pyridine from Water using Toluene as entrainer

We study the separation of the minimum temperature homoazeotropic binary mixture Water – Pyridine. According the Rodriguez-Donis *et al.* (2002) and Skouras (2004, 2005b), the separation is possible using a heterogeneous entrainer. Toluene (intermediate boiling, non-selective entrainer) is added to the mixture, forming a minimum temperature homoazeotrope with Pyridine and a minimum

temperature heteroazeotrope with Water. In this paper, we study the open operation of a batch rectifier with a decanter at the top in which the accumulation (depletion) of the phases is allowed.

6.1 Feasibility analysis

Three simple distillation (residue curve) regions exist with the Water – Toluene heteroazeotrope being the unstable nodes in each region and the stable node being the pure vertexes (Figure 2). The mixture belongs to the Serafimov's class 3.0-2 (122 by Matsuyama and Nishimura classification) (Kiva *et al.*, 2003). The distillation boundaries are strongly curved and tangent to the vapour line at the heteroazeotrope, like any residue curve in the VLLE region. The maps are computed with RegSolResidue® (ProSim, 2005) and drawn with TernaryVisualization® (ProSim, 2005), a free and versatile tool for drawing ternary diagrams available at ProSim's website.

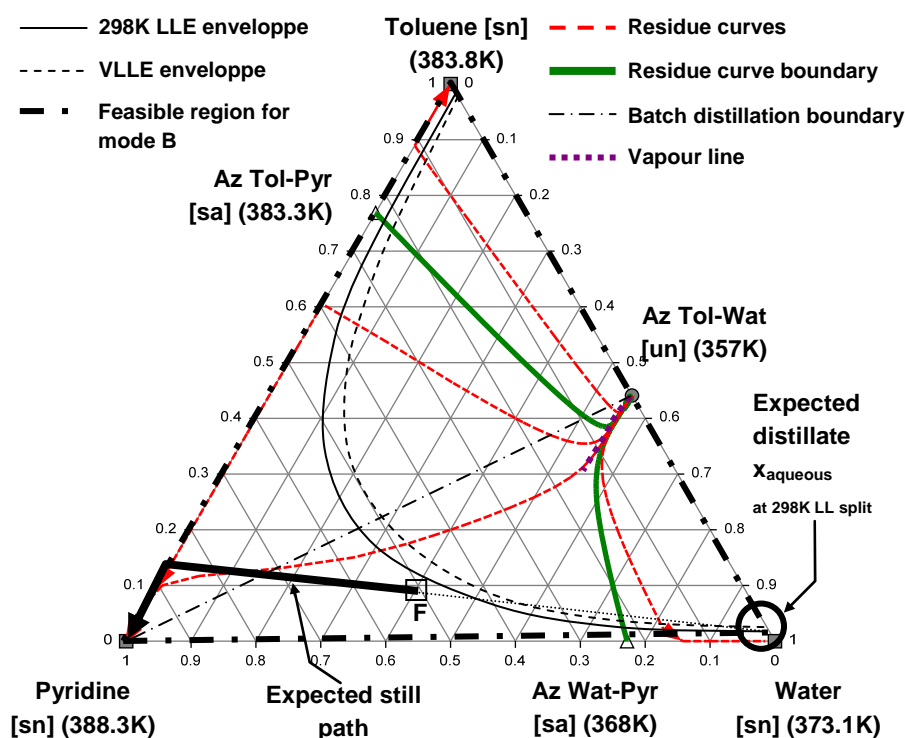


Figure 2. Water/Pyridine/Toluene residue curve map and feasibility region

The NRTL thermodynamic model parameters are given in Table 5. The same set of parameters is used to compute VLLE in the column and 298K LLE in the decanter. The three minimum boiling temperature azeotropes predicted by the NRTL model (55.90% Water – 44.10% Toluene at 357.0K; 76.9%Toluene – 23.1% Pyridine at 383.0K and 77.2% Water – 22.8% Pyridine at 368.0K) are in excellent agreement with the diverse experimental data in the literature ([52.3 to 55.8%] Water – [47.7

to 44.2%] Toluene at [357.2 to 357.6K]; [77.5 to 80.8%] Toluene – [22.5 to 19.2%] Pyridine at [383.2 to 383.4K] and [75.0 to 76.7%] Water – [25.0 to 23.3%] Pyridine at [364.7 to 367.7K]) (Gmehling *et al.*, 1994)

Table 5. VLL and LL Thermodynamic parameters (liquid: NRTL; gas: ideal gas)

Parameter value (cal/mol)	A_{ijO}	A_{jiO}	α_{ijO}	A_{ijT}	A_{jiT}	α_{ijT}
Water – Toluene	3809.1	2776.3	0.2	21.182	-7.3179	0
Water – Pyridine	1779.18	416.162	0.6932	0	0	0
Toluene - Pyridine	264.64	-60.34	0.2992	0	0	0

For NRTL: $g_{ij}-g_{ji}=A_{ijO}+A_{ijT} \cdot (T-273.15)$; $g_{ji}-g_{ii}=A_{jiO}+A_{jiT} \cdot (T-273.15)$; $\alpha_{ij}=\alpha_{ijO}+\alpha_{ijT} \cdot (T-273.15)$

During the heterogeneous batch rectification process, removal of the aqueous phase in the decanter is expected and reflux of either the non-aqueous phase or a combination of both decanter phases is possible. In this work, the whole non-aqueous decanter phase is refluxed. This operating Mode is called Mode II by Skouras (2004, 2005a) who described elegantly the heterogeneous batch distillation process issue and feasibility in complement to Rodriguez-Donis *et al.* (2002). According to Modla *et al.* (2003), Lang and Modla (2005), Skouras (2004) and Skouras *et al.* (2005a), the initial charge composition must be above the line Pyridine – decanter aqueous phase to make the process feasible. The batch distillation boundary has no impact on Mode II process feasibility (but does on Mode I, see Skouras (2004)). The residue curve/distillation boundaries have no impact on feasibility despite their curvature. However, Rodriguez-Donis *et al.* (2002) and Skouras *et al.* (2005a and 2005b) describe two sets of operation for Mode II in non cyclic operation:

- Strategy A: the entrainer-rich phase level is constant because all entrainer-rich phase entering the decanter is refluxed ($\theta=1$ in Rodriguez-Donis *et al.*, 2002),
- Strategy B: the decanter phases can accumulate ($\theta<1$ in Rodriguez-Donis *et al.*, 2002) according to Skouras *et al.* (2005a).

But Rodriguez-Donis *et al.*, (2002) also show that depletion of the entrainer-rich phase in the decanter ($\theta>1$) can be achieved for open operation. As Strategy B seems more difficult to operate effectively, Strategy A is preferred in this feasibility analysis and the expected still path is shown on Figure 2.

6.2. Optimisation problem setting

The column has 16 plates (incl. decanter). Initial charge of 100 moles with molar fractions [Water: 0.4; Toluene: 0.1; Pyridine: 0.5] is placed in the still. Decanter and plate's holdup are constant and equal to 5 and 1 moles respectively. All plate efficiencies are set to unity. Decanter is subcooled to 298K. Column pressure is 1 atm and the pressure drop of the column is 0.05 atm. The process consists of three tasks: filling, infinite reflux and distillation (Water phase removal).

The optimisation problem aims at minimising overall costs and satisfying two molar composition inequality constraints:

- $h_1(x_{\text{Water}}) > 0.992$ in the distillate tank at the process end.
- $h_2(x_{\text{Pyridine}}) > 0.95$ in the still at the process end.

Costs c_1 , c_2 , c_4 , and c_5 (Table 1) are used with arbitrary even cost factors not detailed here.

Five optimisation variables are defined: entrainer load (F_E); heat duty (Q_b/R_∞) and task duration (t/R_∞) for the infinite reflux task; heat duty (Q_b/Dist) and task duration (t/Dist) for the distillate removal task.

Tolerances in the constraints are set to 0.001. For the GA, the initial population equals 100 to ensure efficient sampling of the five dimensions space. GA stop criterion equals 0.1. For the SQP, centred gradients are used. Influence of costs factors and optimiser parameters are not considered in this paper.

6.3 Results and discussion

6.3.1. Optimisation results

Results of the optimisation are given in Table 6. The initial point corresponds to guessed values of the optimisation variables. Its simulation does satisfy the constraints h_1 and h_2 on purpose, but within tolerance for $h_1(x_{\text{Water}})$ and because of this constraint h_1 , the penalized objective function f_p value (meaningful only for GA optimisation) is greater than the objective function f because the penalty Q_1° factor for h_1 is proportional to $1/(0.001^2)$. In the case, not shown here, that the initial point does not satisfy any constraint (is far from an optimal solution) only the GA finds a solution while the SQP does not, hinting at the robustness of the GA in the particular optimisation framework we have implemented.

Table 6. Heterogeneous batch distillation optimisation results

	initial point	SQP	GA	SQP after GA
F_E (kg)	2	1.954	0.866	0.806
Q_b/R_∞ (kcal/hr)	3000	2998	1212	1209
t/R_∞ (hr)	0.2	0.154	0.043	0.026
$Q_b/Dist$ (kcal/hr)	3000	3000	1437	1433
$t/Dist$ (hr)	0.6	0.533	0.647	0.617
Objective function f	155.468	137.182	82.090	77.882
Penalize objective function f_p	183.453	NA	82.090	NA
$h_1(x_{Water})$	-4.24E-04	-7.10E-05	8.9E-04	1.4E-03
$h_2(x_{Pyridine})$	5.38E-03	9.70E-03	9.1E-03	-5.0E-04
Water purity	0.9916	0.9919	0.9929	0.9934
Pyridine purity	0.9554	0.9597	0.9591	0.9495
Water recovery	100%	100%	95%	93%
Pyridine recovery	82%	82%	85%	87%
Gain	0%	12%	47%	50%

For results in Table 6, the SQP improvement of initial conditions is slight. GA ends after 10 population generations but the after the first generation, the objective function has already improved to $f=f_p=90.03$ with a mean value $f=128.3$ and $f_p=1.0 \cdot 10^6$ indicating a wide sampling of the solution space. The optimal solution is already found after the 4th generation; the remaining generations intending to smooth the population so as to satisfy the GA convergence criteria. An important reduction of the heat duty is observed along with a reduction of the entrainer load. SQP improvement of the GA solution is acceptable.

Of course, results are dependant of the cost factors and problem setting. Indeed, for the separation considered, the entrainer load can be much lower to ensure a feasible separation (see skouras, 2004). When done with a cost of entrainer c_4 25 times greater than other costs, the optimiser logically finds a best entrainer load equal to 0.294 kg, but heating required is greater. Besides, for a given purity, $Q_b/Dist$ and $t/Dist$ are linked: heating more implies less time to obtain as much Water.

On this particular problem and on all problems of batch distillation process optimisation we have performed, the SQP does not perform well when the initial point is infeasible, whereas the GA is always able to find a suitable solution to the problem. In fact, SQP should be used on a feasible

solution like the final result of a GA run. This indicates that the GA should always be run first; unless a specific tuning on a feasible solution is sought.

6.3.2. Optimal process simulation

The still, distillate and top vapour paths for the optimal solution of the SQP optimisation done after the GA (last column of Table 4) are reported in Figure 3. The evolution of the liquid composition profile of the column and that of the liquid vapour equilibrium arrow for the top tray are also displayed.

Rigorous simulation results differ from the feasibility analysis described above, clearly showing the impact of the hypothesis of the feasibility analysis (composition profiles approximated by residue curves, infinite number of stage).

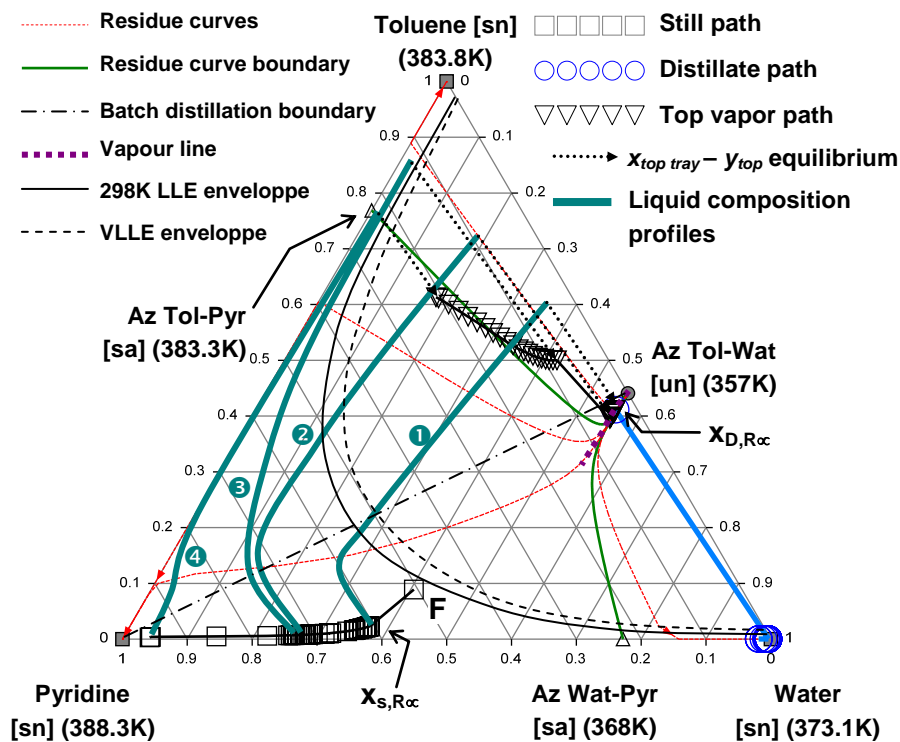


Figure 3. Composition paths and profiles for the optimal separation process of Water – Pyridine using Toluene.

The process total time amounts to 33 min, including 1min 35s of infinite reflux (R_{∞}) operation. Unlike the feasibility analysis predictions, after R_{∞} (liquid composition profile 1), y_{top} is not at the heteroazeotrope Water – Toluene because of the real column features with a finite number of trays and finite holdup on the trays. Like the feasibility analysis predictions, the liquid –liquid split is maintained in the decanter during the whole distillate removal task: x_{Water} starts at 99.28% and ends at 98.6%. Overall x_{Water} is greater than 99.2% as required. After infinite reflux, the decanter split ratio

between the entrainer-rich and the Water-rich phase sets the levels of each phases and is roughly equal to the split ratio at the heteroazeotrope.

After 18 min, y_{top} is further from the heteroazeotrope but still on the vapour line, because the top tray liquid composition is still in the vapour – liquid – liquid region (liquid composition profile 2). But 1 min later, y_{top} leaves the vapour line because the top tray is no longer in the vapour – liquid – liquid region (liquid composition profile 3). As a result, the decanter split ratio increases in favour of the entrainer-rich phase but as no accumulation of this phase is permitted in the constant level decanter, so that the reflux ratio increases to compensate for the increase of the split ratio whereas the distillate flowrate decreases in parallel. In the meanwhile, the still composition is driven towards Pyridine.

A closer look at the still path shows that it is not heading towards the Pyridine – Toluene edge as predicted before for a Mode II / Strategy A operation ($\theta=1$, no accumulation in the decanter), but rather is heading towards the Pyridine – Water edge, much like a Mode II / Strategy B operation mode (accumulation of phases in the decanter / $\theta<1$). As the decanter level is constant, the reason for such behaviour comes from the reflux composition that moves along the entrainer-rich side of the 298K LL envelope whereas the Toluene molar fraction in the reflux decreases accordingly. Such a decrease is equivalent to a $\theta<1$ operation / decrease in the amount of Toluene refluxed. It demonstrates that the feasibility analysis predictions have to be adjusted for real operation in a real column and that Mode II / Strategy B operation can be achieved practically without phase accumulation in the decanter.

At the process end (liquid composition profile 4), the still composition nears the Pyridine vertex but as expected by the Mode II / Strategy A overall operation, it heads towards the Pyridine – Toluene edge, as $x_{Toluene}$ increases slightly. The final still content in Pyridine equals 95% but a longer operation enables to reach 99.1% while reducing the final mean distillate content in Water to 98.2% because the instantaneous distillate composition goes up the 298K liquid – liquid envelope away from the Water – Toluene edge.

7. Case Study two. Separation of Methyl Acetate from Chloroform using Benzene as entrainer

We study the separation of the maximum temperature homoazeotropic binary mixture Methyl Acetate – Chloroform using Benzene as homogeneous, heavy entrainer (solvent) forming no new azeotrope.

This separation requires a sequence of two homogeneous batch distillation columns labelled Seq1 and Seq2 (Rodrigues-Donis *et al.*, 2001a). The offcut – Seq1 tank of the Seq1 column is used as the

feed of the Seq2 column. The optimisation problem considered is simple and has no real process operation signification. But it demonstrates clearly the capability of the optimisation software architecture to optimize several sequential independent sets of differential algebraic equations (DAE), each modelling a batch distillation column; with independent constraints and clearly described transition between the sets of DAE. No such example has been published to our best knowledge.

7.1 Feasibility analysis

7.1.1. Residue curve map

As shown in Figure 4, the addition of the entrainer Benzene adds no new azeotrope. Two simple distillation regions exist. In both regions the maximum boiling azeotrope Methyl Acetate – Chloroform is the saddle and the Benzene vertex is the stable node. Methyl Acetate and Chloroform are unstable nodes. The mixture belongs to the Serafimov's class 1.0-2 (400 by Matsuyama and Nishimura classification) (Kiva *et al.*, 2003). The distillation region boundary (a stable separatrix) is strongly curved and ends at the Benzene vertex tangentially to the edge Chloroform – Benzene.

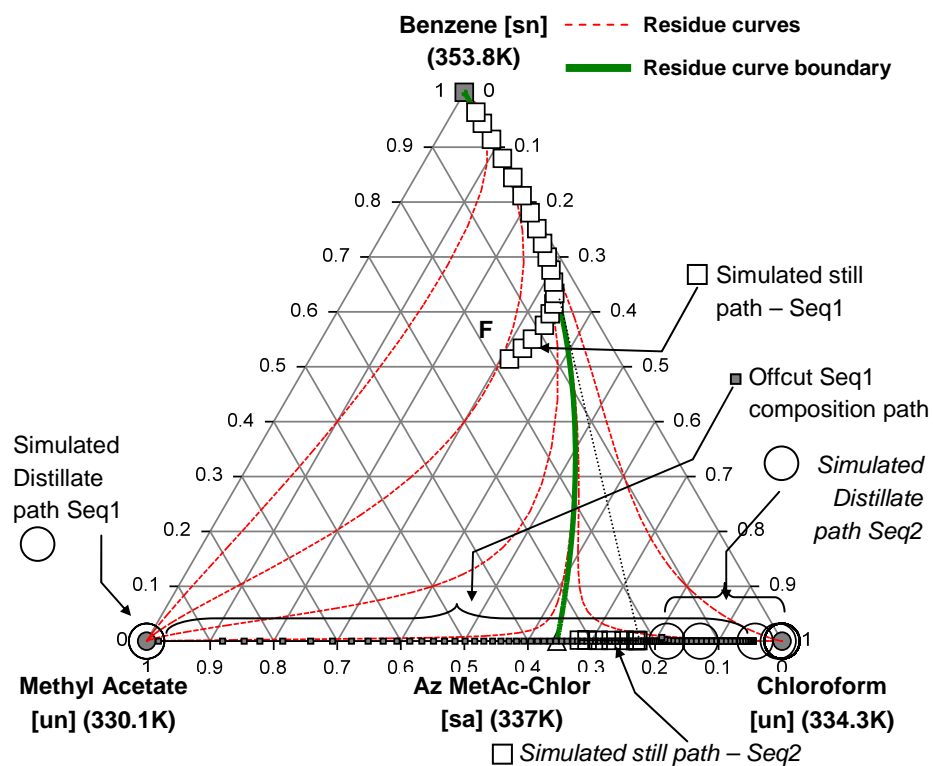


Figure 4. MethylAcetate/Chloroform/Benzene residue curve map. Expected still paths and distillate for each column Seq1 and Seq2 of the homogeneous batch distillation column sequence

The NRTL binary parameters are given in Table 7. The maximum boiling temperature azeotrope predicted by the NRTL model (35.4% Methyl Acetate – 64.6% Chloroform at 337.0K) is in excellent agreement with the diverse experimental data in the literature ([31.4 to 35.2%] Methyl Acetate – [68.6 to 64.8%] Chloroform at [337.6 to 337.9K]) (Gmehling *et al.*, 1994).

Table 7. VLL Thermodynamic parameters (liquid: NRTL; gas: ideal gas)

Parameter value (cal/mol)	A_{ij}	A_{ji}	α_{ij}
<i>Methyl Acetate – Chloroform</i>	-664.023	324.738	0.3051
<i>Methyl Acetate – Benzene</i>	327.357	-109.04	0.2985
<i>Chloroform – Benzene</i>	577.5901	-659.1768	0.3038

For NRTL: $g_{ij}-g_{ji}=A_{ij}$; $g_{ji}-g_{ii}=A_{ji}$;

According to Rodriguez-Donis *et al.* (2001a), the process for such a ternary system with a concave region Methyl Acetate – binary azeotrope – Benzene requires two rectification columns, labelled Seq1 and Seq2. The pioneering works of Doherty's group (Van Dongen and Doherty, 1985; Bernot *et al.*, 1990, 1991) help understand the composition evolution in the still and in the distillate cuts. Seq1 column is fed in the concave region. With a high number of stages and reflux ratio, the still path moves straight away from the first cut that is located at the lowest boiling temperature point of the simple distillation region, namely Methyl Acetate. Once the still composition reaches the curved boundary, the pure Methyl Acetate distillate tank is closed. Indeed, the still composition follows then the curved boundary towards the highest boiling temperature point of the simple distillation region, namely Benzene. Then, the distillate composition also shifts suddenly on the binary edge Methyl Acetate – Chloroform because according to Doherty's group works and as is readily shown by still composition differential equation, it is set by the tangent to the still path. This is recovered in the offcut tank of the first column Seq1 which should ideally be exempt of any entrainer (Benzene). Seq2 Column is fed with this binary mixture offcut tank of Seq1 and consists ideally in a binary distillation. The lowest boiling temperature component (Chloroform) is obtained as distillate whereas the still composition ends on the azeotrope point. It ends as soon as the Chloroform average purity drops below specification in the distillate tank. At last, the final still content in the Seq2 column still contains the same binary mixture

that the initial charge of seq1. So this sequence does effectively split the binary azeotrope Methyl Acetate – Chloroform but the recovery yield is not optimum. Other processes with other kind of entrainer exist with better separation efficiency (Rodriguez-Donis *et al.*, 2001a, 2001b, Skouras *et al.*, 2005b). The expected still and distillation paths are illustrated on figure 4.

7.1.2. Batch distillation column transitions

Feeding the second batch distillation column with the offcut tank of the first column is what we call a column transition. Having described all feasibility rules in former publications, we formalized column transition in parallel with the setting of the optimization software architecture, in order to be able to optimize batch distillation sequences. Notice that no tank recycle is considered in the following.

From the knowledge of inputs and outputs of rectification or stripper or middle vessel batch distillation column, column transitions are described. Possible distillation tanks are the boiler (all configurations), the top drum (condenser-decanter in a heterogeneous column, homogeneous drum in a stripper column), distillate tanks (rectification and middle vessel), residue removal tanks (stripper), middle-vessel tanks (middle-vessel). Complexity arises when considering heterogeneous batch distillation process because all or only one of the phases in a heterogeneous tank may be concerned by the transition.

The description of a column transition consists in linking an output transition (Table 8) to an input transition (Table 9), which is transferring all the information of an output tank to input tank(s). This information is the usual quantity, average composition, temperature and pressure.

Output transitions are:

Table 8. Output Transitions for batch distillation columns (rectification, stripper or middle vessel)

Number	Name	Description
11	<i>OutStillAll</i>	<i>All the still content</i>
12	<i>OutCondAll</i>	<i>All the condenser content</i>
13	<i>OutDecAll</i>	<i>All the decanter content</i>
14	<i>OutDecLight</i>	<i>Only the decanter Light phase is concerned</i>
15	<i>OutDecHeavy</i>	<i>Only the decanter heavy phase is concerned</i>
16	<i>OutMVAll</i>	<i>All the middle vessel content</i>
17	<i>OutMVLigh</i>	<i>Only the middle vessel light phase is concerned</i>
18	<i>OutMVHeavy</i>	<i>Only the middle vessel heavy phase is concerned</i>
19	<i>OutTankAll</i>	<i>All the tank content, concern distillate or residue tank</i>

Input transitions are less numerous but for a stripper, it is recommended to split the charge between the still and the top condenser tank:

Table 9. Input Transitions for batch distillation columns (rectification, stripper or middle vessel)

Number	Name	Description
21	<i>InStillAll</i>	<i>The charge is totally fed in the still</i>
22	<i>InCondpart</i>	<i>The charge is partially fed in the still and in the condenser/top drum (split ratio must be given).</i>
23	<i>InMVPart</i>	<i>The charge is totally fed in the middle vessel</i>
24	<i>InTankAll</i>	<i>The charge is totally fed in the tank</i>

In the case study two, the Seq1 and Seq2 rectification columns are linked by a column transition made of output transition 19 (OutTankAll) (by assigning the source column and the identification number of the tank) and input transition 21 (InStillAll).

7.2. Optimisation problem setting

The Seq1 column has 50 plates. Initial charge of 200 moles with molar fractions [Methyl Acetate: 0.177; Chloroform: 0.323; Benzene: 0.5] is placed in the still. Plate's holdup is constant and equal to 0.16 moles respectively. Heat duty equals 1500 W. All plate efficiencies are set to unity. Column pressure is 1 atm and no pressure drop is considered. Seq1 operation consists of four tasks: filling, infinite reflux, distillate (Methyl Acetate removal), offcut removal.

The Seq2 column has 30 plates. Initial charge is placed in the still and is the offcut tank of Seq1 column. Plate's holdup is constant and equal to 0.23 moles respectively. Heat duty equals 1500 W. All plate efficiencies are set to unity. Column pressure is 1 atm and no pressure drop is considered. Seq2 operation consists of three tasks: filling, infinite reflux, distillate (Chloroform removal).

The same NRTL thermodynamic model is used for both Seq1 and Seq2 columns. Notice that optimisation can work with thermodynamic models different in each column.

The process operation proceeds in five tasks described in Table 10, along with the switching/stopping events.

Table 10. Two homogeneous batch distillation columns sequence operation tasks and main events

Column	Task	Reflux ratio	Distillate tank	Task switching / stopping event
Seq1	1 – Filling (initial entrainer amount *)			
	2 - Start-up	<i>infinite</i>	<i>N.A.</i>	<i>t = 0.1 hr.</i>
	3 - Recovery of Methyl Acetate (A)	<i>Initially 20 *</i>	<i>Dist – Seq1</i>	<i>A_{Dist – Seq1} > 20 mol</i>
	4 - Recovery of binary mixture Offcut	<i>30</i>	<i>Offcut – Seq1</i>	<i>x_{Benzene, Offcut – Seq1} > 0.001</i>
<i>transition</i>	<i>Offcut – Seq1 tank is fed to Seq2 boiler</i>			
Seq2	5 - Filling			
	6 - Start-up	<i>Infinite</i>	<i>N.A.</i>	<i>t = 0.1 hr.</i>
	7 - Recovery of Chloroform (B)	<i>Initially 30 *</i>	<i>Dist – Seq2</i>	<i>B_{Dist – Seq2} = 27 mol</i>

* Optimisation variable

The choice of the task events enabling switching to the next task is governed by a preliminary search so that they enable to get a stable composition and temperature profile in the columns (task2 and 6), so that they can be reached with reasonable values of reflux ratio (task 3 and 7), and so that they ensure that almost no entrainer pollutes the charge on column Seq2 (task4).

The optimisation problem aims at minimising overall costs and satisfying two molar composition inequality constraints located on different batch columns:

- $h_1(x_{\text{MethylAcetate,Dist – Seq1}}) > 0.99$ in the distillate tank Dist – Seq1 at the process end.
- $h_2(x_{\text{Chloroform,Dist – Seq2}}) > 0.99$ in the distillate tank Dist – Seq2 at the process end .

Costs c_1 , c_2 , c_4 , and c_5 (Table 1) are used with arbitrary even cost factors not detailed here.

Three optimisation variables are defined: entrainer load in Seq1 (F_E); reflux ratio in the recovery of Methyl Acetate ($R_3/\text{Dist – Seq1}$) and reflux ratio in the recovery of Chloroform ($R_7/\text{Dist – Seq2}$).

Tolerances in the constraints are set to 0.001. For the GA, the initial population equals 100 to ensure efficient sampling of the five dimensions space. GA stop criterion explained above equals 0.01.

Influence of costs factors are not considered in this paper.

7.3 Results and discussion

7.3.1. Optimisation results

Results of the optimisation are given in Table 11. The initial point simulation does satisfy the constraints h_1 and h_2 on purpose.

Table 11. Homogeneous batch distillation sequence optimisation results

	initial point	GA
$F_E - \text{Seq1(kg)}$	7.81	8.27
$R_{\text{task3}/\text{Dist}} - \text{Seq1 (-)}$	20.00	17.73
$R_{\text{task7}/\text{Dist}} - \text{Seq2 (-)}$	30.00	9.43
Objective function f	1700.83	1430.71
$h_1(X_{\text{MetAc, Dist}} - \text{Seq1})$	0.87E-02	0.606E-02
$h_2(X_{\text{Chloroform, Dist}} - \text{Seq2})$	0.99E-02	-0.105E-03
Methyl Acetate purity in Dist – Seq1	0.9987	0.99606
Chloroform purity in Dist – Seq2	0.9999	0.98995
Gain	0%	15%

The purpose of the case study two is fulfilled, that is to demonstrate that the optimisation software architecture is capable of optimising sequential independent DAE sets representing different columns. Even though this is not a meaningful case study from the process operation point of view as time, among other variables is not optimized, the optimization results hint at noteworthy process operation features. The purity constraints are satisfied within tolerances, showing that the two distillation column sequence enables to separate the initial binary mixture into pure compounds. The overall gain in the objective function around 15% is significant, mostly due to the reduced operation time of Seq2 operation because of the lower reflux ratio, and despite the supplementary cost induced by more entrainer in Seq1. More entrainer was expected because of the boundary curvature: according to feasibility analysis rule aforementioned, the offcut tank composition on the binary edge is set by the tangent to the still composition path. This later should therefore reach the boundary close enough to the benzene vertex so that the mean composition in the offcut tank is rich enough in chloroform.

The GA reaches convergence after 28 generations. Like case study one, the first generation best solution shows already a great improvement of the initial point (objective function $f = 1474$). But contrary to case study one (10 generations and optimal solution not improved after the 4th generation), another significant improvement of the best solution is done at the 15th generation (objective function f

= 1430) which is the final optimal solution proposed. This shows again the efficiency of the sampling of the solution space by the GA.

7.3.1. Optimal process simulation

The optimal process is simulated with BatchColumn® and the composition paths in the still and in the distillate tanks are displayed on figure 5.

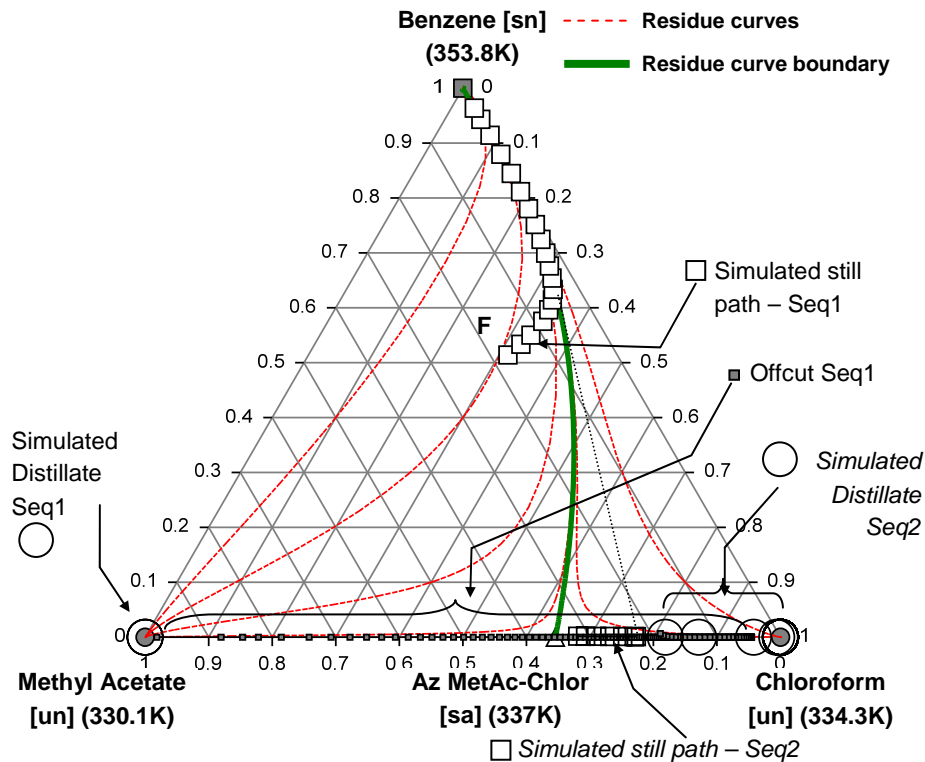


Figure 5. MethylAcetate/Chloroform/Benzene residue curve map. Simulated still paths and distillate for each column Seq1 and Seq2 of the homogeneous batch distillation column sequence with optimal parameters

The simulated composition paths match the feasibility predictions, but for a few differences due to the use of real column features (plate holdup, finite reflux and number of plate). The most significant difference concerns the still path during the recovery of the Dist – Seq1 that does not go straight to the boundary but is slightly incurved towards the benzene vertex. The higher is the reflux in this task, the straighter is the still path. As a consequence, the distillate composition does not stay at the Methyl Acetate vertex but moves on the binary edge Methyl Acetate – Chloroform (indistinguishable on the figure). For the same reason, the offcut composition path starts close to the Methyl Acetate vertex rather than close to the Chloroform one as expected from the feasibility analysis.

8. Conclusion

An optimisation framework coupling stochastic GA and deterministic SQP approaches has been devised and suited for batch distillation processes, homogeneous or heterogeneous, single batch column or batch columns sequence. Validation is done on two case studies with real batch distillation column features and thermodynamics. Validation on case study one (a double task single rectifier heterogeneous batch process for the separation of Water- Pyridine with Toluene) with five optimisation variables shows that the use of GA followed by an SQP is the recommended choice. Validation on case study two (a two homogeneous batch distillation column sequence for the separation of Methyl Acetate – Chloroform with Benzene) demonstrates the capability of the optimisation framework to handle sequential different sets of differential algebraic equation sets, thus showing that it is readily suited for the optimisation of the novel batch distillation processes described in the literature (Rodriguez-Donis *et al.*, 2001a, 2001b, 2002; Modla *et al.*, 2003, Skouras *et al.*, 2005b).

As careful weighting of the optimisation variables shows, such a powerful optimisation tool should be used by users well acquainted with the process expected behaviour. But in reward, it also enables the user to perceive process operation features and process parameter sensitivity.

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Acknowledgements

This work was performed in collaboration with ProSim SA (Toulouse, France), and supported by the french environment and energy agency (ADEME).

Figure Caption

Figure 1. Optimisation software architecture and overall resolution scheme

Figure 2. Water/Pyridine/Toluene residue curve map and feasibility region

Figure 3. Composition paths and profiles for the optimal separation process of Water – Pyridine using Toluene.

Figure 4. MethylAcetate/Chloroform/Benzene residue curve map. Expected still paths and distillate for each column Seq1 and Seq2 of the homogeneous batch distillation column sequence

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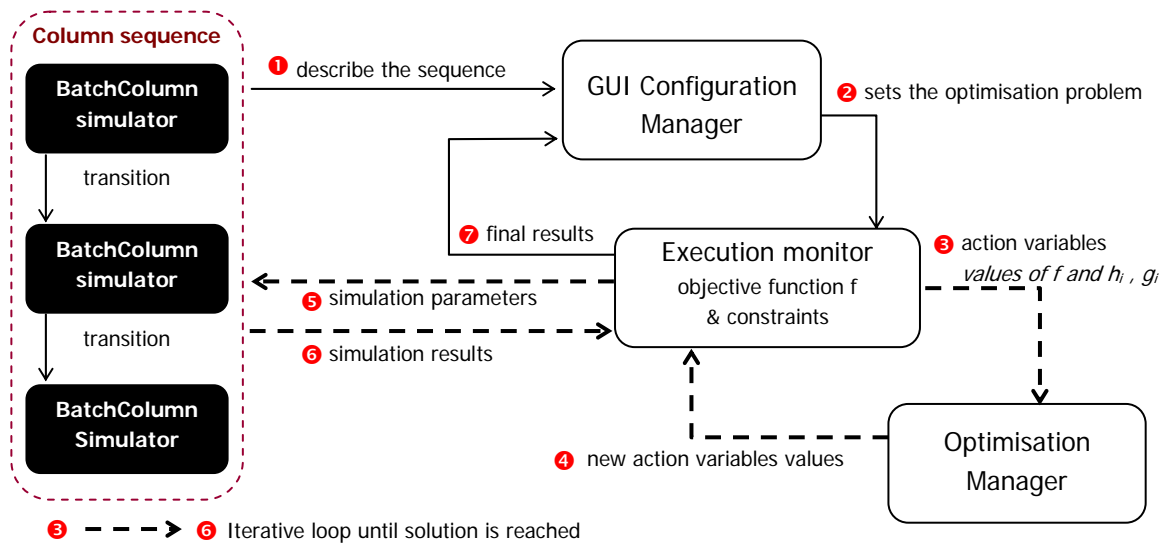


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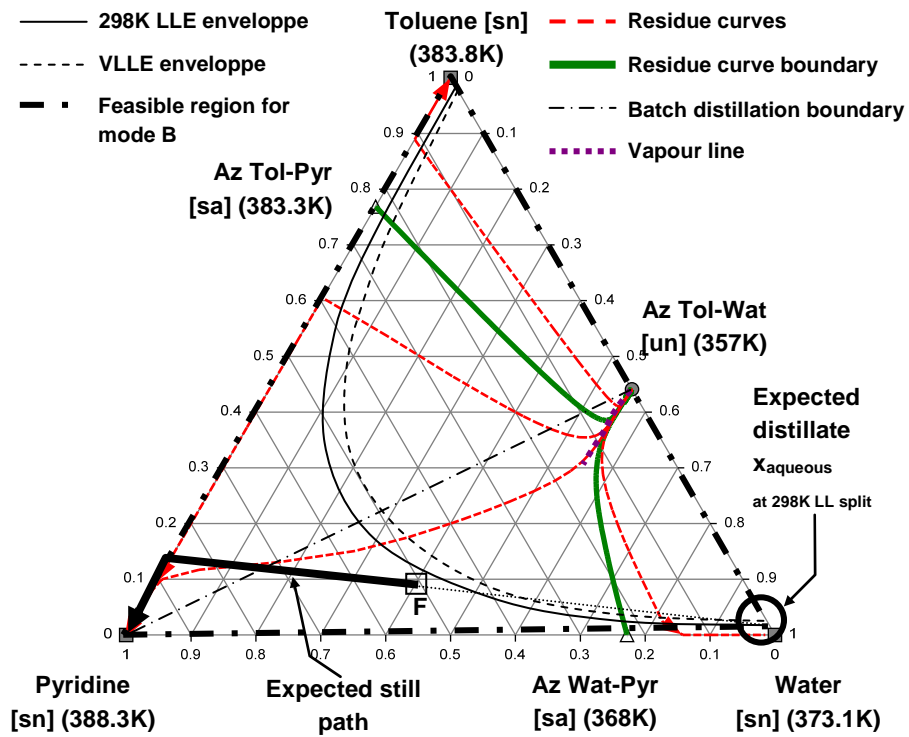


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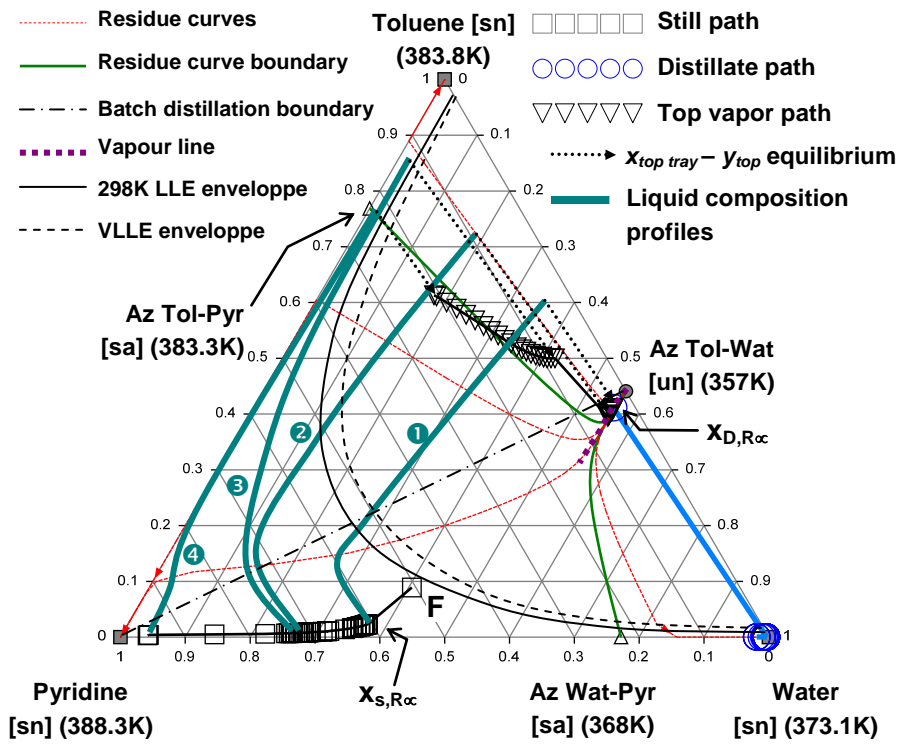


Figure 3. Composition paths and profiles for the optimal separation process of Water – Pyridine using Toluene.

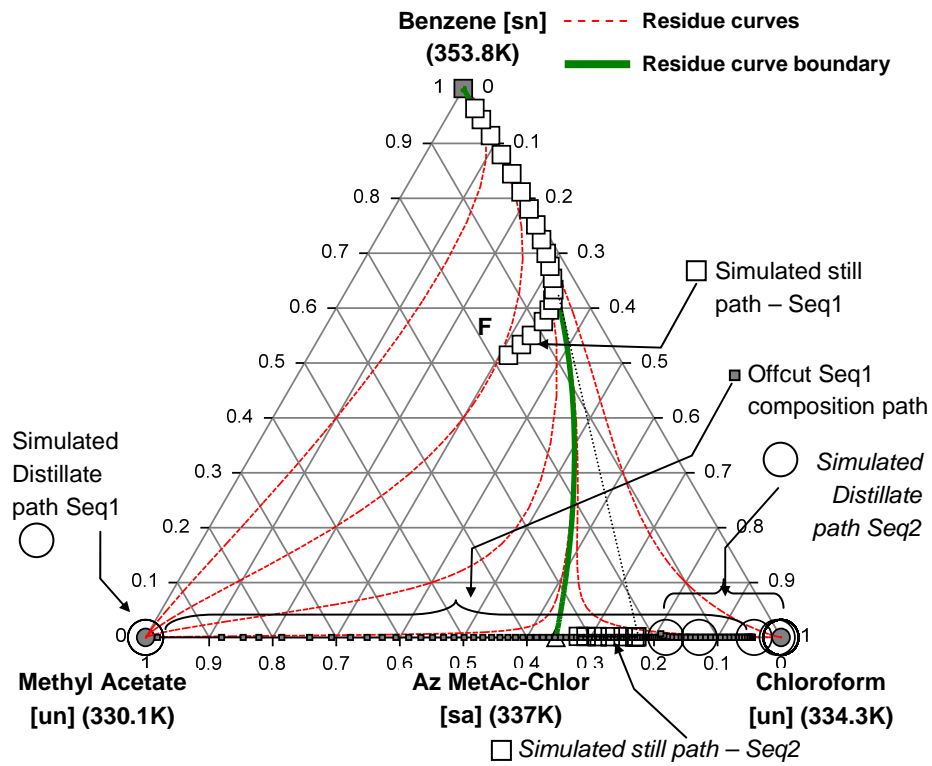


Figure 4. MethylAcetate/Chloroform/Benzene residue curve map. Expected still paths and distillate for each column Seq1 and Seq2 of the homogeneous batch distillation column sequence

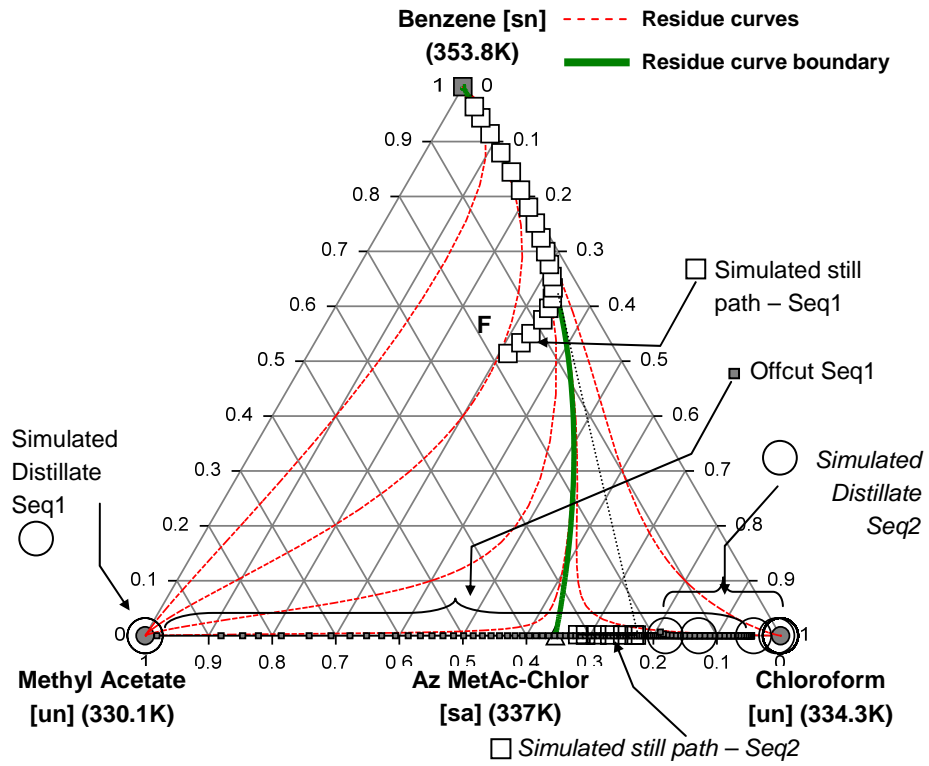


Figure 5. MethylAcetate/Chloroform/Benzene residue curve map. Simulated still paths and distillate for each column Seq1 and Seq2 of the homogeneous batch distillation column sequence with optimal parameters

Table Caption

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Table 1. Economical cost functions taken into account in the objective function

cost function	$f = \sum_1^6 c_i$	object	expression	used variable
c_1		immobilisation	$c_1 = a_1 \cdot t + b_1$	t = total separation duration
c_2		energy	$c_2 = a_2 \cdot Q$	Q = total required energy
c_3		load	$c_3 = a_3 \cdot L$	L = global column load
c_4		entrainer	$c_4 = a_4 \cdot E$	E = entrainer amount added initially
c_5		column treatment	$c_5 = a_5 \cdot R + b_5$	R = residual column load
c_6		tanks treatments	$c_6 = \sum_{k=1}^{n_T} a_6^k \cdot T_k + b_6^k$	T_k = final load of each of the n_T tanks (including still)

Table 2. Available optimisation variables

optimisation variable (* available for each task i)	
<i>Entrainer load</i>	<i>Task duration</i> *
<i>Boiling duty</i> *	<i>Reflux ratio of light phase</i> * [£]
<i>Subcooling temperature</i> *	<i>Reflux ratio of heavy phase</i> * [£]

£: in case of homoazeotropic distillation, these optimisation variables are replaced by the usual reflux ratio.

Table 3. Parameter sensitivity analysis on the GA optimisation results

Genetic Algorithm	Initial conditions	Reference set	Initial population		Selection rate	Mutation rate	Penalized weighting factor
			10	1000			
					0.8	0.01	10^3
t_{switch} (hr)	1	1.42	1.38	1.57	1.20	1.51	1.66
R_1	0.5	0.82	0.74	0.82	0.82	0.83	0.82
R_1	0.5	0.88	0.86	0.89	0.89	0.89	0.90
Objective function f = - A recovery yield	0.99	4.267	4.872	4.348	4.260	4.170	4.400
$h_1(x_A)$ (>0.950)	0.501	0.952	0.841	0.950	0.953	0.959	0.945
Population number	-	28	20	30	9	26	20
Objective function evaluation number	-	1723	120	18814	956	1521	1247

Table 4. Parameter sensitivity analysis on the SQP optimisation results

Sequential Quadratic Programming	GA Reference set	Best SQP result	Epsx
t_{switch} (hr)	1.42	1.695	1.697
R_1	0.82	0.821	0.822
R_1	0.88	0.897	0.897
Objective function $f = -A$ recovery yield	4.267	4.356	4.354
$h_1(x_A)$ (>0.950)	0.952	0.95020	0.95000
Constraint evaluation number	28*	99	203
Objective function evaluation number	1723	148	262
Stop condition	-	A2	A3 (A1 condition satisfied)

* Population number

Table 5. VLL and LL Thermodynamic parameters (liquid: NRTL; gas: ideal gas)

Parameter value (cal/mol)	A_{ij0}	A_{ji0}	α_{ij0}	A_{ijT}	A_{jiT}	α_{ijT}
Water – Toluene	3809.1	2776.3	0.2	21.182	-7.3179	0
Water – Pyridine	1779.18	416.162	0.6932	0	0	0
Toluene - Pyridine	264.64	-60.34	0.2992	0	0	0

For NRTL: $g_{ij}-g_{jj}=A_{ij0}+A_{ijT} \cdot (T-273.15)$; $g_{ji}-g_{ii}=A_{ji0}+A_{jiT} \cdot (T-273.15)$; $\alpha_{ij}=\alpha_{ij0}+\alpha_{ijT} \cdot (T-273.15)$

Table 6. Heterogeneous batch distillation optimisation results

	initial point	SQP	GA	SQP after GA
F_E (kg)	2	1.954	0.866	0.806
Q_b/R_∞ (kcal/hr)	3000	2998	1212	1209
t/R_∞ (hr)	0.2	0.154	0.043	0.026
$Q_b/Dist$ (kcal/hr)	3000	3000	1437	1433
$t/Dist$ (hr)	0.6	0.533	0.647	0.617
Objective function f	155.468	137.182	82.090	77.882
Penalize objective function f_p	183.453	NA	82.090	NA
$h_1(X_{Water})$	-4.24E-04	-7.10E-05	8.9E-04	1.4E-03
$h_2(X_{Pyridine})$	5.38E-03	9.70E-03	9.1E-03	-5.0E-04
Water purity	0.9916	0.9919	0.9929	0.9934
Pyridine purity	0.9554	0.9597	0.9591	0.9495
Water recovery	100%	100%	95%	93%
Pyridine recovery	82%	82%	85%	87%
Gain	0%	12%	47%	50%

Table 7. VLL Thermodynamic parameters (liquid: NRTL; gas: ideal gas)

Parameter value (cal/mol)	A_{ij}	A_{ji}	α_{ij}
<i>Methyl Acetate – Chloroform</i>	-664.023	324.738	0.3051
<i>Methyl Acetate – Benzene</i>	327.357	-109.04	0.2985
<i>Chloroform – Benzene</i>	577.5901	-659.1768	0.3038

For NRTL: $g_{ij}-g_{ji}=A_{ij}$; $g_{ji}-g_{ii}=A_{ji}$;

Table 8. Output Transitions for batch distillation columns (rectification, stripper or middle vessel)

Number	Name	Description
11	<i>OutStillAll</i>	<i>All the still content</i>
12	<i>OutCondAll</i>	<i>All the condenser content</i>
13	<i>OutDecAll</i>	<i>All the decanter content</i>
14	<i>OutDecLight</i>	<i>Only the decanter Light phase is concerned</i>
15	<i>OutDecHeavy</i>	<i>Only the decanter heavy phase is concerned</i>
16	<i>OutMVAll</i>	<i>All the middle vessel content</i>
17	<i>OutMVLigh</i>	<i>Only the middle vessel light phase is concerned</i>
18	<i>OutMVHeavy</i>	<i>Only the middle vessel heavy phase is concerned</i>
19	<i>OutTankAll</i>	<i>All the tank content, concern distillate or residue tank</i>

Table 9. Input Transitions for batch distillation columns (rectification, stripper or middle vessel)

Number	Name	Description
21	<i>InStillAll</i>	<i>The charge is totally fed in the still</i>
22	<i>InCondpart</i>	<i>The charge is partially fed in the still and in the condenser/top drum (split ratio must be given).</i>
23	<i>InMVPart</i>	<i>The charge is totally fed in the middle vessel</i>
24	<i>InTankAll</i>	<i>The charge is totally fed in the tank</i>

Table 10. Two homogeneous batch distillation columns sequence operation tasks and main events

Column	Task	Reflux ratio	Distillate tank	Task switching / stopping event
Seq1	1 – Filling (initial entrainer amount *)			
	2 - Start-up	<i>infinite</i>	<i>N.A.</i>	<i>t = 0.1 hr.</i>
	3 - Recovery of Methyl Acetate (A)	<i>Initially 20 *</i>	<i>Dist – Seq1</i>	<i>A_{Dist-Seq1} > 20 mol</i>
	4 - Recovery of binary mixture Offcut	<i>30</i>	<i>Offcut – Seq1</i>	<i>x_{Benzene, Offcut-Seq1} > 0.001</i>
<i>transition</i>	<i>Offcut – Seq1 tank is fed to Seq2 boiler</i>			
Seq2	5 - Filling			
	6 - Start-up	<i>Infinite</i>	<i>N.A.</i>	<i>t = 0.1 hr.</i>
	7 - Recovery of Chloroform (B)	<i>Initially 30 *</i>	<i>Dist – Seq2</i>	<i>B_{Dist-Seq2} = 27 mol</i>

* Optimisation variable

Table 11. Homogeneous batch distillation sequence optimisation results

	initial point	GA
$F_E - \text{Seq1}(\text{kg})$	7.81	8.27
$R2/\text{Dist} - \text{Seq1} (-)$	20.00	17.73
$R5/\text{Dist} - \text{Seq2} (-)$	30.00	9.43
Objective function f	1700.83	1430.71
$h_1(X_{\text{MetAc}}, \text{Dist} - \text{Seq1})$	0.87E-02	0.606E-02
$h_2(X_{\text{Chloroform}}, \text{Dist} - \text{Seq2})$	0.99E-02	-0.105E-03
Methyl Acetate purity in Dist – Seq1	0.9987	0.99606
Chloroform purity in Dist – Seq2	0.9999	0.98995
Gain	0%	15%